REMARKS

Status of the Claims:

Claims 1 – 28 are currently pending.

Claims 1 – 28 are currently rejected.

Claims 1, 3 – 10, 12, 13, 15 – 20, 22, 24, 25, 27 and 28 are currently amended.

Claims 29 – 32 are new.

Amendments to the Claims:

No new matter has been introduced by way of the claim amendments.

Claim 1 is presently amended to recite an acid solvent forming a solution of dispersed carbon nanotubes, rather than an acidic medium as previously recited. Support that the acidic medium is an acid solvent may be found in at least paragraphs [0037], [0044] (solubility), [0056] and [0060]. In addition, a limitation that the acid solvent is selected from the group consisting of a superacid and an oxoacid has been incorporated. Support for this amendment may be found in at least original claims 3 and 4. Claim 1 is also amended in the functionalzing step to clarify that functionalizing takes place using a functionalizing agent, and functionalizing takes place while the carbon nanotubes are dispersed in the acid solvent. Support for a functionalizing agent may be found in at least original claim 7. Support that functionalizing takes place while the carbon nanotubes are dispersed in the acid solvent may be found in at least paragraphs [0030], [0056] and [0060] The functionalizing step is elsewhere amended for stylistic and clarity purposes. In addition, claim 1 is amended in the preamble for stylistic purposes, and labels a) and b) have been deleted from the claim.

Claim 3 is presently amended to add a Markush group for the superacid. Support for the amendment may be found in at least paragraph [0033] and original claim 20.

Claim 4 is presently amended to be commensurate with the amendments to claim 1. In addition, claim 4 is presently amended to correct a minor grammatical error in the Markush group.

Claim 5 is presently amended to be commensurate with amended claim 1.

Claim 6 is presently amended to be commensurate with amended claim 1 and to also recite that the acid solvent further comprises a persulfate species.

Claims 7 – 9 are presently amended for stylistic purposes.

Claim 10 is presently amended to change the verb to comprises.

Claim 12 is presently amended into the form of a proper method claim to recite a step further comprising the method of claim 1.

Claim 13 is presently amended to be commensurate with amended claim 1. In addition, labels a) and b) have been deleted from the claim.

Claim 16 is presently amended to recite a superacid solvent, rather than a superacid medium as previously recited. Support that the superacid medium is a superacid solvent may be found in at least paragraphs [0037], [0044] (solubility), [0056] and [0060]. Claim 16 is also amended to clarify that the dispersion is of single-wall carbon nanotubes. Claim 16 is also amended to clarify that the aniline species and the nitrite species form a diazonium species. Support for this amendment may be found in at least original claim 9. Claim 16 is also amended to clarify that reacting the single-wall carbon nanotubes with the diazonium species occurs while dispersed in the superacid solvent. Support for this amendment may be found in at least paragraphs [0030], [0056] and [0060]. In addition, claim 16 is amended in the preamble for stylistic purposes, and labels a) and b) have been deleted from the claim.

Claim 17 is presently rewritten as a step further comprising the method of claim 16. In addition, amended claim 17 recites oxidatively purifying rather than oxidatively treating. Support for oxidative purification may be found in at least paragraph [0051].

Claim 18 is presently amended to recite sorting the single-wall carbon nanotubes according to a property prior to dispersing. Support for amended claim 18 may be found in at least paragraph [0032].

Claim 19 is presently amended for stylistic purposes.

Claim 20 is presently amended to be commensurate in scope with amended claim 16.

Claim 22 is presently amended to recite that the superacid solvent further comprises a radical source. Support for this amendment may be found in at least the original claim.

Claim 24 is presently amended for stylistic purposes and to clarify that the dispersion is heated and stirred.

Claim 25 is presently amended for purposes of clarity and to make the claim commensurate with prior amendments. Support for the amendments may be found in at least the original claim. Claim 25 is also amended in the preamble for stylistic purposes, and labels a), b) and c) have been deleted from the claim.

Claim 27 is presently amended for purposes of clarity and to make the claim commensurate with prior amendments. Support for the amendments may be found in at least the original claim. Claim 27 is also amended in the preamble for stylistic purposes, and labels a) and b) have been deleted from the claim.

New claim 29 is supported by at least paragraphs [0037] and [0047].

New claims 30 and 31 are supported by at least paragraph [0046].

New claim 32 is supported by at least paragraph [0035].

I. Objection to the Drawings

The Examiner has objected to Figures 6, 7, 9a and 10 due to their quality. Office Action page 2, item 1. Applicants submit replacement drawings sheets in compliance with 37 CFR 1.84(b) to address the objection to these Figures. Applicants also submit replacement drawing sheets for Figures 4 and 5 to improve the quality of those Figures.

In addition, the Examiner has objected to Figure 2 due to improper numbering of views. Office Action page 2, item 1. In a telephone interview between Applicants' representative and the Examiner conducted on June 28, 2010, the Examiner acknowledged that the objection to claim 2 due to improper numbering of the views was in error and agreed to withdraw the objection. However, in order to better clarify Figure 2, Applicants have redrawn Figure 2 with

anilines **1a** – **12a** presented in sequential order. In addition, Applicants have amended the specification in paragraph [0045] to clarify that anilines **7a** – **12a** may also be used in the embodiments illustrated in Scheme 1 (FIGURE 1).

II. 35 U.S.C. § 112, Second Paragraph Rejections

Claims 4, 13, 25 and 27 stand rejected under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter regarded as the invention. Office Action page 3, item 3. Regarding claim 4, the Examiner alleges that the claim contain improper Markush terminology. Regarding claims 13, 25 and 27, the Examiner alleges that the numbering of steps a), b) and c) within the claims renders the claims indefinite in view of steps a) and b) recited in preceding claims.

Applicants have amended claim 4 to delete 'and' before HNO_3. Applicants respectfully assert that this amendment places the Markush group into proper format and request that the 35 U.S.C. § 112, second paragraph, rejection be withdrawn.

Applicants have amended claims 1 and 13 and claims 16, 25 and 27 to remove all the reference letters cited therein. In view of the removal of the reference letters, Applicants respectfully assert that the claims are compliant with 35 U.S.C. § 112, second paragraph, and request that that the rejection be withdrawn.

III. 35 U.S.C. § 102 Rejections

III.1 Standard of Review

The standard of review for establishing anticipation under 35 U.S.C. § 102 is set forth as follows: "[a] claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference." *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987); MPEP § 2131. "Anticipation requires the presence in a single prior art reference disclosure of each and every element of the claimed invention, *arranged as in the claim*." *W.L. Gore & Assoc. v. Garlock, Inc.*, 721 F.2d 1540, 1554 (Fed. Cir. 1983), *cert. denied*, 469 U.S. 851 (1984). Moreover, it is not enough that the prior art reference disclose all the claimed elements in isolation. Rather, as stated by the Federal Circuit, "[a]nticipation requires the presence in a

single prior art reference disclosure of each and every element of the claimed invention, *arranged as in the claim*." *Id; Lindemann Maschienenfabrik GMBH v. American Hoist & Derrick Co.*, 730 F.2d 1452, 1458 (Fed. Cir. 1984) (emphasis added).

III.2 Claims 1, 2, 4, 5, 7, 8, 10, 12 and 15 Rejected Under 35 U.S.C. § 102(e) Over Cooper

Claims 1, 2, 4, 5, 7, 8, 10, 12 and 15 stand rejected under 35 U.S.C. § 102(e) as being anticipated by United States Patent Application Publication 2007/0084797 (hereinafter, *Cooper*). Office Action page 4, item 9. Applicants respectfully traverse the rejection of these claims.

III.2.1 Examiner's Grounds for Rejection

The Examiner alleges that *Cooper* teaches a method in which carbon nanotubes are dispersed in an acidic medium to form dispersed carbon [nanotubes] and then functionalizing the dispersed carbon nanotubes by covalently attaching functional groups to the sidewalls to yield sidewall functionalized carbon nanotubes. The Examiner alleges that substantially exposed sidewalls are inherently taught by *Cooper*, since this reference allegedly teaches the same process and materials. With regard to the dependent claims, the Examiner alleges that single-wall and multi-wall carbon nanotubes, H_2SO_4, HNO_3, functionalizing agents (particularly diazonium species and salts), post-processing steps, and the claimed degree of functionalization are taught.

III.2.2 Claims 1, 2, 4, 5, 7, 8, 10, 12 and 15 are Not Anticipated by Cooper

Applicants respectfully assert that claims 1, 2, 4, 5, 7, 8, 10, 12 and 15 are not anticipated by *Cooper*, since this reference fails to expressly or inherently teach all limitations of amended independent claim 1. Claim 1 is presently amended to clarify that functionalizing the carbon nanotubes occurs <u>while the carbon nanotubes are dispersed in the acid solvent</u>. Applicants respectfully assert that this new limitation of claim 1 and others are not expressly or inherently taught by *Cooper* as set forth hereinafter.

Foremost, claim 1 requires that the carbon nanotubes are functionalized on their <u>sidewalls</u>. In contrast, *Cooper* expressly teaches that the carbon nanotubes are functionalized with organic or inorganic groups <u>on their ends</u> (see *Cooper*, paragraph [0052]). Hence, *Cooper* does not anticipate the claim in this regard.

In addition, Applicants respectfully assert that *Cooper* does not teach dispersing carbon nanotubes in an acid solvent **and** subsequent sidewall functionalization of the carbon nanotubes while in the acid solvent, as required by claim 1. In paragraph [0117] (cited by the Examiner as providing support for an acid medium; Office Action page 4, item 10), *Cooper* teaches washing the carbon nanotubes with a strong oxidizing agent such as an acid to remove amorphous carbon and iron impurities. Washing with an acid to purify carbon nanotubes does not result in dispersion or functionalization of the carbon nanotubes. Evidence to this effect is provided by Liu, et al., "Fullerene Pipes", Science, 280:1998, pp. 1253-1256 (hereinafter, *Liu*), which is supplied as Appendix I of this paper (for example, see page 1253, Col. 3, first paragraph of *Liu*).

Even though the acid washing taught by *Cooper* does **not** result in a carbon nanotube dispersion, *Cooper* provides further express teachings clarifying that an acid solution of carbon nanotubes is not utilized in any of the embodiments described therein, as discussed hereinafter. In addition to these further teachings, *Cooper* is silent regarding functionalization, particularly sidewall functionalization, in an acid solvent.

As a first example, in paragraph [0121] *Cooper* teaches pouring a dispersion of carbon nanotubes in an organic solvent onto fiber paper and then evaporating the solvent. Hence, in this embodiment, *Cooper* cannot anticipate the claim limitation of sidewall functionalizing dispersed carbon nanotubes in an acid solvent, since *Cooper* does not teach an acid solvent. Further, the organic solvent has been removed by evaporation, and there is no teaching of functionalization in a solvent of any kind.

As a second example, in paragraphs [0123] and [0124] (cited by the Examiner as providing support for an acid medium), *Cooper* teaches coating a metal oxide surface of a mesh using dispersed carbon nanotubes in a liquid. *Cooper* teaches that the surface is annealed in vacuum at 1000°C, and that the carbon nanotubes may be optionally treated in a mixture of nitric and sulfuric acids to create carboxyl functional groups on the carbon nanotubes (see *Cooper*, paragraph [0124]). As an initial point of distinction regarding this embodiment, *Cooper* does not teach that the liquid used for coating the mesh is an acid solvent. Secondly, *Cooper* is silent regarding functionalization, particularly sidewall functionalization, either before or after coating of the mesh. Although *Cooper* also makes reference to a mixture of nitric and sulfuric acids in paragraph [0124] as a means for introducing carboxyl groups, *Cooper* does not teach that the

mixture of nitric and sulfuric acids is used for coating the metal oxide surface. More importantly, however, treatment of carbon nanotubes in a mixture of nitric and sulfuric acids results in opening of the carbon nanotubes and formation of carboxylic acid groups on their ends, not on their sidewalls as required by claim 1. Evidence to this effect is supplied by *Liu* (see *Liu*, page 1254, Col. 2 inclusive). In conclusion, the aforementioned embodiment of *Cooper* fails to anticipate the present claim limitations.

As a third example, in paragraph [0126] *Cooper* teaches filtering an organic solvent dispersion of carbon nanotubes (with ultrasonication) and depositing the carbon nanotubes on a substrate. Hence, in this embodiment, *Cooper* cannot anticipate the claim limitation of sidewall functionalizing dispersed carbon nanotubes in an acid solvent, since *Cooper* does not teach an acid solvent.

As a final example, in paragraph [0131] (cited by the Examiner as providing support for an acid medium), *Cooper* teaches reacting a dispersion of carbon nanotubes in an acid solution. In paragraph [0131] *Cooper* expressly teaches that the carbon nanotubes are cut and their opened ends have carboxyl ions grafted thereto. Such a process is akin to that described by *Liu*. Since this embodiment of *Cooper* teaches carbon nanotubes functionalized on their ends, not on their sidewalls, *Cooper* does not anticipate the present claim limitations.

In summary, *Cooper* fails to teach the combination of dispersing carbon nanotubes in an acid solvent and subsequent sidewall functionalization of the dispersed carbon nanotubes in the acid solvent. Since all limitations of claim 1 are not expressly or inherently taught by *Cooper*, claim 1 is not anticipated by this reference. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from patentable claim 1 and are not anticipated by *Cooper* for at least the same reasons. *In re Fine,* 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988). Therefore, Applicants respectfully request that the Examiner's rejection of claims 1, 2, 4, 5, 7, 8, 10, 12 and 15 under 35 U.S.C. § 102(e) be withdrawn.

III.3 Claims 1 – 5, 7 and 12 – 15 Rejected Under 35 U.S.C. § 102(e) Over Khabashesku

Claims 1 – 5, 7 and 12 – 15 stand rejected under 35 U.S.C. § 102(e) as being anticipated by United States Patent 7,125,533 (hereinafter, *Khabashesku*). Office Action page 6, item 16. Applicants respectfully traverse the rejection of these claims.

III.3.1 Examiner's Grounds for Rejection

The Examiner alleges that *Khabashesku* teaches a method in which carbon nanotubes are dispersed in an acidic medium to form dispersed carbon [nanotubes] and then functionalizing the dispersed carbon nanotubes by covalently attaching functional groups to the sidewalls to yield sidewall functionalized carbon nanotubes. The Examiner alleges that substantially exposed sidewalls are inherently taught by *Khabashesku*, since the same process and materials are allegedly taught. With regard to the dependent claims, the Examiner alleges that single- and multi-wall carbon nanotubes, superacids, H_2SO_4, H_3PO_4, HNO_3, carbon radicals, post-processing steps, isolation by filtering, water as a solvent, and the claimed degree of functionalization are taught.

III.3.2 Claims 1 – 5, 7 and 12 – 15 are Not Anticipated by Khabashesku

Applicants respectfully assert that claims 1 – 5, 7 and 12 – 15 are not anticipated by *Khabashesku*, since all limitations of amended independent claim 1 are not expressly or inherently taught by the cited reference. Amended claim 1 requires that sidewall functionalization of the dispersed carbon nanotubes takes place <u>while the dispersed carbon nanotubes are in an acid solvent</u>. *Khabashesku*, in contrast, does not teach sidewall functionalization that takes place while the carbon nanotubes are dispersed in an acid solvent. Specifically, *Khabashesku* teaches in Col. 7, line 66 through Col. 8, line 21 that the carbon nanotubes are oxidatively heated and then treated with an acid <u>to remove metal impurities</u>. *Khabashesku* goes on to expressly teach that "<u>**the nanotubes are filtered and washed to remove the acid from the nanotubes**</u>" (see *Khabasheku*, Col. 8, lines 14 – 16, emphasis added). *Khabashesku* uses these oxidatively heated and acid-treated carbon nanotubes in subsequently described embodiments. As noted above, <u>washing</u> with an acid does not disperse or sidewall functionalize carbon nanotubes. Furthermore, since the acid is <u>removed</u> before the carbon nanotubes are used in subsequent teachings of *Khabashesku*, it follows that this reference fails to teach sidewall functionalization of carbon nanotube <u>in an acid solvent</u>.

Although *Khabashesku*, teaches dicarboxylic acid acyl peroxides for functionalizing carbon nanotubes in Col. 12, line 60 – Col. 13, line 28, the dicarboxylic acid acyl peroxide is a <u>reactant</u>, not a solvent used for dispersing the carbon nanotubes (for example, see *Khabashesku*,

Col. 19, lines 41 – 59). *Khabashesku* in no way teaches that a dicarboxylic acid acyl peroxide may disperse carbon nanotubes.

In view of the foregoing remarks, Applicants respectfully assert that all limitations of amended independent claim 1 are not expressly or inherently taught by *Khabashesku*, and claim 1 is therefore not anticipated by this reference. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from patentable claim 1 and are not anticipated by *Khabashesku* for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claims 1 – 5, 7 and 12 – 15 under 35 U.S.C. § 102(e) be withdrawn.

III.4 Claims 1, 2, 4, 5, 7 – 10, 12 and 15 Rejected Under 35 U.S.C. § 102(b) Over Dyke

Claims 1, 2, 4, 5, 7 – 10, 12 and 15 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Dyke, et al., "Solvent-Free Functionalization of Carbon Nanotubes", J. Am. Chem. Soc., 125:2003, pp. 1156-1157 (hereinafter, *Dyke*). Office Action page 8, item 27. Applicants respectfully traverse the rejection of these claims.

III.4.1 Examiner's Grounds for Rejection

The Examiner alleges that *Dyke* teaches a method comprising dispersing carbon nanotubes in an acidic medium to form dispersed carbon [nanotubes] and then functionalizing the dispersed carbon nanotubes by covalently attaching functional groups to the sidewalls to yield sidewall functionalized carbon nanotubes. The Examiner alleges that substantially exposed sidewalls are inherently taught by *Dyke*, since the same process and materials are allegedly taught. Regarding the dependent claims, the Examiner alleges that single- and multi-wall carbon nanotubes, H_2SO_4, in-situ generation of a diazonium salt, post-processing steps and the claimed degree of functionalization are taught.

III.4.2 Claims 1, 2, 4, 5, 7 – 10 and 12 are Not Anticipated by Dyke

Applicants respectfully assert that claims 1, 2, 4, 5, 7 – 10, and 12 are not anticipated by *Dyke*, since all limitations of amended independent claim 1 are not expressly or inherently taught by the cited reference. In particular, amended claim 1 requires dispersing carbon nanotubes in an acid <u>solvent</u>. Dispersing, in turn, forms dispersed carbon nanotubes having substantially exposed sidewalls. *Dyke*, in contrast, teaches a **<u>solvent-free</u>** process for functionalizing carbon nanotubes

(see *Dyke*; page 1156, Col. 1, first paragraph and Scheme 1). Although Scheme 1 of *Dyke* teaches acids H_2SO_4 or AcOH (acetic acid) according to one set of reaction conditions, the taught acids are <u>reactants</u>, not a <u>solvent</u> for dispersing carbon nanotubes. For example, *Dyke* teaches that acids are used with $NaNO_2$ to form compound **1** taught therein (see *Dyke*; page 1157, Col. 1, 5th full paragraph).

In addition, *Dyke* teaches on page 1156, Col. 1, 2nd paragraph that the reaction mixture is a <u>paste</u>. Such a paste does not contain dispersed carbon nanotubes according to the teachings of *Dyke*. Specifically, *Dyke* provides further teachings in Figure 3 and page 1157, Col. 2, 1st paragraph that it is the mechanical forces of mixing that cause deroping of carbon nanotubes in a carbon nanotube bundle. *Dyke* in no way teaches that an acid solvent creates dispersed carbon nanotubes having substantially exposed sidewalls, especially since this reference expressly teaches a **<u>solvent-free</u>** process.

In view of the foregoing remarks, Applicants respectfully assert that all limitations of amended independent claim 1 are not expressly or inherently taught by *Dyke*, and claim 1 is therefore not anticipated by this reference. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from patentable claim 1 and are not anticipated for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claims 1, 2, 4, 5, 7 – 10, 12 and 15 under 35 U.S.C. § 102(b) be withdrawn.

III.5 Claims 1, 6 and 15 Rejected Under 35 U.S.C. § 102(e) Over Niu

Claims 1, 6 and 15 stand rejected under 35 U.S.C. § 102(e) as being anticipated by United States Patent 7,070,753 (hereinafter, *Niu*). Office Action page 9, item 34. Applicants respectfully traverse the rejection of these claims.

III.5.1 Examiner's Grounds for Rejection

The Examiner alleges that *Niu* teaches a method comprising dispersing carbon nanotubes in a persulfate species to form dispersed carbon [nanotubes] and then functionalizing the dispersed carbon nanotubes by covalently attaching functional groups to the sidewalls to yield sidewall functionalized carbon nanotubes. The Examiner alleges that substantially exposed sidewalls are inherently taught by *Dyke*, since the same process and materials are allegedly

taught. Regarding the dependent claims, the Examiner alleges that the claimed degree of functionalization is taught.

III.5.2 Claims 1, 6 and 15 Are Not Anticipated by Niu

Applicants respectfully assert that claims 1, 6 and 15 are not anticipated by *Niu*, since all limitations of amended independent claim 1 are not expressly or inherently taught by this reference. As amended, claim 1 requires that the acid solvent is selected from the group consisting of a superacid and an oxoacid. *Niu*, in contrast, teaches oxidation of carbon nanotubes using peroxygen compounds such as, for example, organic peroxyacids, inorganic peroxyacids, and organic hydroperoxides (see *Niu*, Abstract and claim 1). *Niu* is silent on other types of acids, particularly superacids and oxoacids. Peroxyacids are characterized by O-OH functional groups, whereas superacids and oxoacids are characterized by simple acid OH functional groups. Therefore, *Niu* teaches different acids than those required by claim 1.

In view of the foregoing remarks, Applicants respectfully assert that all limitations of amended independent claim 1 are not expressly or inherently taught by *Niu*, and claim 1 is therefore not anticipated by this reference. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from patentable claim 1 and are not anticipated for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claims 1, 6 and 15 under 35 U.S.C. § 102(e) be withdrawn.

IV 35 U.S.C. § 103 Rejections

IV.1 Standard of Review

For rejections made under 35 U.S.C. § 103(a), all claim limitations must be taught or suggested by the prior art to establish obviousness. *In re Royka,* 490 F.2d 981, 180 U.S.P.Q. 580 (C.C.P.A. 1974). Furthermore, "[r]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness". *KSR Int'l Co. v. Teleflex Inc.*, 127 S.Ct. 1727, 1741 (2007) citing with approval *In re Kahn*, 441 F.3d 977, 988 (CA Fed. 2006). Likewise, in issuing rejections under 35 U.S.C. § 103(a), the Examiner must consider an

invention and the prior art as a whole in accordance with the requisite *Graham* factual inquiries. M.P.E.P. § 2141; *Ruiz v. A.B. Chance Co.* 69 U.S.P.Q.2d 1686, 1690 (Fed. Cir. 2004).

Furthermore, "[a] rationale to support a conclusion that a claim would have been obvious is that all the claimed elements were known in the prior art and one skilled in the art could have combined the elements as claimed by known methods with no change in their respective functions, and the combination would have yielded nothing more than predictable results to one of ordinary skill in the art." M.P.E.P. § 2143.02. Although "[o]bviousness does not require absolute predictability...at least some degree of predictability is required." *Ibid.* "The *KSR* Court noted that obviousness cannot be proven merely by showing that the elements of a claimed device were known in the prior art; it must be shown that those of ordinary skill in the art would have had some 'apparent reason to combine the known elements in the fashion claimed.'" *Ex parte Whalen*, 89 USPQ2d at 1084 citing *KSR Int'l Co. v. Teleflex Inc.*, 127 S.Ct. at 1741.

IV.2 Statement Regarding Non-Common Ownership

Applicants acknowledge the Examiner's statement regarding non-common ownership. Office Action page 11, item 39. Applicants are presently unaware of any non-common ownership but will promptly inform the Examiner should they become aware of any ownership change.

IV.3 Claim 15 Rejected Under 35 U.S.C. § 103(a) Over Khabashesku

Claim 15 stands rejected under 35 U.S.C. § 103(a) as being unpatentable over *Khabashesku*. Office Action page 11, item 40. Applicants respectfully traverse the rejection of this claim.

IV.3.1 Examiner's Grounds for Rejection

The Examiner applies *Khabashesku* as set forth hereinabove and further alleges that the functionalization amount is a result effective variable that one of ordinary skill in the art would expect to produce different properties in the product.

IV.3.2 Claim 15 is Not Obvious

Applicants respectfully assert that claim 15 is not obvious, since claim 1, from which claim 15 depends, is not obvious. As set forth hereinabove, amended independent claim 1 is not anticipated by *Khabashesku*. For at least the same reasons as those set forth hereinabove, claim 1 is also not obvious, since all limitations are not taught or suggested by this reference. Specifically, since *Khabashesku* teaches <u>removal</u> of the acid used for <u>washing</u> the carbon nanotubes, this reference fails to teach or suggest sidewall functionalization of carbon nanotubes in an acid solvent.

In view of the foregoing remarks, Applicants respectfully assert that amended independent claim 1 is not obvious in view of *Khabashesku*. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from non-obvious claim 1 and are not obvious for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claim 15 under 35 U.S.C. § 103(a) be withdrawn.

IV.4 Claim 15 Rejected Under 35 U.S.C. § 103(a) Over Dyke

Claim 15 stands rejected under 35 U.S.C. § 103(a) as being unpatentable over *Dyke*. Office Action page 11, item 42. Applicants respectfully traverse the rejection of this claim.

IV.4.1 Examiner's Grounds for Rejection

The Examiner applies *Dyke* as set forth hereinabove and further alleges that the functionalization amount is a result effective variable that one of ordinary skill in the art would expect to produce different properties in the product.

IV.4.2 Claim 15 is Not Obvious

Applicants respectfully assert that claim 15 is not obvious, since claim 1, from which claim 15 depends, is not obvious. As set forth hereinabove, amended independent claim 1 is not anticipated by *Dyke*. For at least the same reasons as those set forth hereinabove, claim 1 is also not obvious, since all limitations are not taught or suggested by this reference. In fact, *Dyke* expressly teaches away from amended independent claim 1, since *Dyke* expressly requires a <u>solvent-free</u> process for functionalizing carbon nanotubes.

In view of the foregoing remarks, Applicants respectfully assert that amended independent claim 1 is not obvious in view of *Dyke*. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from non-obvious claim 1 and are not obvious for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claim 15 under 35 U.S.C. § 103(a) be withdrawn.

IV.5 Claim 15 Rejected Under 35 U.S.C. § 103(a) Over Cooper

Claim 15 stands rejected under 35 U.S.C. § 103(a) as being unpatentable over *Cooper*. Office Action page 12, item 44. Applicants respectfully traverse the rejection of this claim.

IV.5.1 Examiner's Grounds for Rejection

The Examiner applies *Cooper* as set forth hereinabove and further alleges that the functionalization amount is a result effective variable that one of ordinary skill in the art would expect to produce different properties in the product.

IV.5.2 Claim 15 is Not Obvious

Applicants respectfully assert that claim 15 is not obvious, since claim 1, from which claim 15 depends, is not obvious. As set forth hereinabove, amended independent claim 1 is not anticipated by *Cooper*. For at least the same reasons as those set forth hereinabove, claim 1 is also not obvious, since all limitations are not taught or suggested by this reference. Specifically, *Cooper* teaches functionalization of carbon nanotubes on their ends, not their sidewalls. Additionally, *Cooper* fails to teach or suggest the combination of dispersing carbon nanotubes in an acid solvent and subsequent sidewall functionalization of the dispersed carbon nanotubes in the acid solvent.

In view of the foregoing remarks, Applicants respectfully assert that amended independent claim 1 is not obvious in view of *Cooper*. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from non-obvious claim 1 and are not obvious for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claim 15 under 35 U.S.C. § 103(a) be withdrawn.

IV.6 Claim 9 Rejected Under 35 U.S.C. § 103(a) Over Cooper in View of Dyke

Claim 9 stands rejected under 35 U.S.C. § 103(a) as being unpatentable over *Cooper* in view of *Dyke*. Office Action page 13, item 46. Applicants respectfully traverse the rejection of this claim.

IV.6.1 Examiner's Grounds for Rejection

The Examiner acknowledges that *Cooper* does not teach that a diazonium species is generated in situ by reaction of an aniline with a nitrite species. However, the Examiner alleges that reaction of an aniline species with a nitrite species is known in the art and used for the functionalization of carbon nanotubes, as evidenced by *Dyke*. Therefore, the Examiner alleges that it would have been obvious to one of ordinary skill in the art to modify *Cooper* with a diazonium species generated *in situ* according to *Dyke.*

IV.6.2 Claim 9 is Not Obvious

Applicants respectfully assert that claim 9 is not obvious, since claim 1, from which claim 9 depends, is not obvious in view of the combined teachings of *Cooper* and *Dyke*. As set forth in more detail hereinabove, neither *Cooper* nor *Dyke* teach or suggest the claim limitation of dispersing carbon nanotubes in an acid solvent or sidewall functionalizing carbon nanotubes therein. Applicants previously established hereinabove that *Cooper* fails to teach or suggest the claim limitation of dispersing carbon nanotubes in an acid solvent, since *Cooper* only teaches washing carbon nanotubes with an acid to purify them. Furthermore, in no embodiments does *Cooper* teach or suggest sidewall functionalizing carbon nanotubes in an acid solvent. *Dyke* fails to remedy the noted deficiencies of *Cooper*, since *Dyke* expressly teaches a solvent-free process for functionalizing carbon nanotubes.

In view of the foregoing remarks, Applicants respectfully assert that amended independent claim 1 is not obvious in view of *Cooper* and *Dyke*. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from non-obvious claim 1 and are not obvious for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claim 9 under 35 U.S.C. § 103(a) be withdrawn.

IV.7 Claim 11 Rejected Under 35 U.S.C. § 103(a) Over Cooper in View of Csuzdi

Claim 11 stands rejected under 35 U.S.C. § 103(a) as being unpatentable over *Cooper* in view of United States Patent 6,600,036 (hereinafter, *Csuzdi*). Office Action page 13, item 50. Applicants respectfully traverse the rejection of this claim.

IV.7.1 Examiner's Grounds for Rejection

The Examiner acknowledges that *Cooper* does not teach a diazonium species generated from a triazene precursor. However, the Examiner alleges that triazene precursors are obvious variants of diazonium salts, as evidenced by *Csuzdi*. Therefore, the Examiner alleges that it would have been obvious to one of ordinary skill in the art to modify *Cooper* with the triazene precursor of *Csuzdi*.

IV.7.2 Claim 11 is Not Obvious

Applicants respectfully assert that claim 11 is not obvious, since claim 1, from which claim 11 depends, is not obvious in view of the combined teachings of *Cooper* and *Csuzdi*. As set forth in more detail hereinabove, *Cooper* fails to teach or suggest the claim limitation of dispersing carbon nanotubes in an acid solvent or sidewall functionalizing carbon nanotubes therein. Applicants previously established hereinabove that *Cooper* fails to teach or suggest the claim limitation of dispersing carbon nanotubes in an acid solvent, since *Cooper* only teaches <u>washing</u> carbon nanotubes with an acid to purify them. Furthermore, in no embodiments does *Cooper* teach or suggest sidewall functionalizing carbon nanotubes in an acid solvent. *Csuzdi* fails to remedy the noted deficiencies of *Cooper*, since *Csuzdi* is silent regarding carbon nanotubes, and more particularly carbon nanotubes dispersed in an acid solvent.

In view of the foregoing remarks, Applicants respectfully assert that amended independent claim 1 is not obvious in view of *Cooper* and *Csuzdi*. Claims 2 – 15 and new claims 29 and 30 depend either directly or indirectly from non-obvious claim 1 and are not obvious for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claim 11 under 35 U.S.C. § 103(a) be withdrawn.

IV.8 Claims 16 – 20 and 22 – 28 Rejected Under 35 U.S.C. § 103(a) Over Khabashesku in View of Cooper and Dyke

Claims 16 – 20 and 22 – 28 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over *Khabashesku* in view of *Cooper* and *Dyke*. Office Action page 14, item 54. Applicants respectfully traverse the rejection of these claims.

IV.8.1 Examiner's Grounds for Rejection

The Examiner alleges that *Khabashesku* teaches a method of a) dispersing single-wall carbon nanotubes in a superacid medium to form a dispersion and b) functionalizing the dispersed carbon nanotubes by covalently attaching functional groups to their sidewalls. The Examiner acknowledges that *Khabashesku* does not teach adding an aniline species and a nitrite species to form a reaction mixture or reaction of the reaction mixture. However, the Examiner alleges that *Cooper* teaches a method of a) dispersing carbon nanotubes in an acidic medium to form dispersed carbon (nanotubes), and b) functionalizing the dispersed carbon nanotubes by covalently attaching functional groups to their sidewalls using diazonium salts. The Examiner alleges that is well known in the art to react an aniline species with a nitrite species to form diazonium species for functionalization of carbon nanotubes, as evidenced by *Dyke*. Therefore, the Examiner alleges that it would have been obvious to one of ordinary skill in the art to modify the process of *Khabashesku* with *in situ* formation of a diazonium species as taught by *Dyke*.

With regard to the dependent claims, the Examiner alleges that oxidatively treated single-wall carbon nanotubes; homogenous length and diameter; filtering; various superacid media; radical sources; benzoyl peroxide; heating and stirring; diluting, filtering and washing; acetone; resuspending and filtering, and the claimed degree of functionalization are taught.

IV.8.2 Claim 16 – 20 and 22 – 28 Are Not Obvious

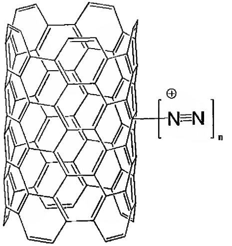
Applicants respectfully assert that claims 16 – 20 and 22 – 28 are not obvious, since independent claim 16 is not obvious in view of the combined teachings of *Khabashesku*, *Cooper* and *Dyke*. In particular, the combined teachings of the cited references fail to teach or suggest a reaction of single-wall carbon nanotubes with a diazonium species that occurs while the single-wall carbon nanotubes are dispersed in a superacid solvent. As discussed in detail hereinabove,

Khabashesku teaches treatment of carbon nanotubes with an acid to remove metal impurities, followed by filtering and washing to remove the acid from the carbon nanotubes. *Khabashesku* in no way teaches or suggests functionalizing single-wall carbon nanotubes while dissolved in an acid solvent.

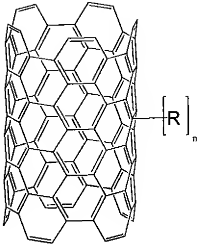
Cooper fails to remedy the noted deficiencies of *Khabashesku*, since *Cooper* also fails to teach or suggest dispersion of single-wall carbon nanotubes in a superacid solvent or functionalization therein. As discussed in more detail hereinabove, *Cooper* only teaches washing the carbon nanotubes with a strong oxidizing agent such as an acid to remove amorphous carbon and iron impurities. As previously asserted by Applicants, washing does not equate to dispersing carbon nanotubes in an acid solvent. In addition, *Cooper* is silent regarding superacids. *Dyke* likewise fails to remedy the deficiencies of *Khabashesku* and *Cooper*, since this reference is similarly silent on superacids and, in fact, expressly teaches a solvent-free process for functionalizing carbon nanotubes. Therefore, *Cooper* and *Dyke* also fail to teach or suggest the claimed superacid dispersion of single-wall carbon nanotubes and reaction with a diazonium species therein.

In addition to the foregoing remarks establishing that the cited references fail to teach or suggest reacting in a superacid solvent, Applicants also respectfully assert that *Cooper* fails to teach or suggest reacting a diazonium species with carbon nanotubes in any solvent, in contrast to the allegations of the Examiner. Specifically, *Cooper* teaches in paragraphs [0049] and [0050] that functionalized carbon nanotubes comprise **organic and/or inorganic compounds** attached to the surface of the carbon nanotubes, and the **organic compounds** may be diazonium salts. Therefore, *Cooper* does not teach or suggest **reaction of** diazonium salts **with** carbon nanotubes. Instead, *Cooper* teaches that the functionalized carbon nanotube products referenced in paragraphs [0049] and [0050] have diazonium groups attached to them. Carbon nanotubes having diazonium salts **attached thereto**, and carbon nanotubes **reacted with** diazonium salts are not the same as shown in Figure 1 below. Specifically, carbon nanotubes having diazonium salts **attached thereto** are characterized by N_2^+ functional groups, whereas carbon nanotubes **reacted with** diazonium salts are characterized by alkyl or aryl groups (R groups) introduced by the diazonium salt and attached to the functionalized carbon nanotube product.

Figure 1



functionalized carbon nanotubes containing diazonium salts attached thereto



carbon nanotubes that were functionalized with a diazonium salt (R=alkyl or aryl)

In view of the foregoing remarks, Applicants respectfully assert that amended independent claim 16 is not obvious in view of *Khabasheskų, Cooper* and *Dyke*. Claims 17 – 28 and new claims 31 and 32 depend either directly or indirectly from non-obvious claim 16 and are not obvious for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claims 16 – 20 and 22 – 28 under 35 U.S.C. § 103(a) be withdrawn.

IV.9 Claim 21 Rejected Under 35 U.S.C. § 103(a) Over Khabashesku in View of Cooper, Dyke and Yu

Claim 21 stands rejected under 35 U.S.C. § 103(a) as being unpatentable over *Khabashesku* in view of *Cooper*, *Dyke* and United States Patent 6,399,202 (hereinafter, *Yu*). Office Action page 18, item 67. Applicants respectfully traverse the rejection of this claim.

IV.9.1 Examiner's Grounds for Rejection

The Examiner applies *Khabashesku*, *Cooper* and *Dyke* as previously set forth hereinabove and further alleges that *Yu* teaches sulfanilic acid. Therefore, the Examiner alleges that it would have been obvious to use sulfanilic acid in modifying the previously cited art.

IV.9.2 Claim 21 Is Not Obvious

Applicants respectfully assert that claim 21 is not obvious, since independent claim 16, from which claim 21 depends, is not obvious. Specifically, the combined teachings of *Khabashesku*, *Cooper* and *Dyke* fail to teach or suggest all limitations of independent claim 16. Applicants' prior remarks to this effect are reiterated ***in toto***. *Yu* fails to remedy the noted deficiencies of *Khabashesku*, *Cooper* and *Dyke*, since, at a minimum, this reference is silent regarding carbon nanotubes. Furthermore, *Yu* fails to teach or suggest any type of dispersion in a superacid solvent, as required by the claim.

In view of the foregoing remarks, Applicants respectfully assert that independent claim 16 is not obvious in view of *Khabashesku*, *Cooper*, *Dyke* and *Yu*. Claims 17 – 28 and new claims 31 and 32 depend either directly or indirectly from non-obvious claim 16 and are not obvious for at least the same reasons. Therefore, Applicants respectfully request that the Examiner's rejection of claim 21 under 35 U.S.C. § 103(a) be withdrawn.

V. Double Patenting

Claims 1, 2, 4, 5, 7 – 10, 15, 16, 20, 24 and 28 stand rejected on the grounds of non-statutory obviousness-type double patenting as being unpatentable over claims 1 – 5, 11, 20 and 25 of commonly-owned United States Patent 7,459,137 (hereinafter, *'137*). Office Action page 19, item 70. Applicants respectfully traverse the instant non-statutory obviousness-type double patenting rejection on the grounds set forth hereinafter.

The claims of the instant double patenting rejection are subject to the one-way test of obviousness set forth in MPEP 804, which requires that the claims defined in the application be anticipated by or obvious variants of the claims defined in the patent. Applicants respectfully assert that amended claims 1, 2, 4, 5, 7 – 10, 15, 16, 20, 24 and 28 fail the one-way obviousness test, since the instant claims, as amended, as not obvious variants over the claims of *'137*. Specifically, the claims of *'137* require that reacting takes place <u>in the absence of a solvent</u>. The claims of the instant application, in contrast, specifically require that reacting takes place when the carbon nanotubes are dispersed in either an oxoacid or superacid solvent. The solvent-free claims of *'137* teach against the acid solvent claims of the instant application. Therefore,

Applicants respectfully assert that the present double patenting rejection is in error and request that the rejection be withdrawn.

CONCLUSIONS

Claims 1 – 32 are now pending in the application. Applicants respectfully submit that claims 1 – 32, as these claims presently stand amended, are in a condition for allowance based on the remarks presented hereinabove.

The Director is hereby authorized to charge any fees or credit any overpayment due to Deposit Account Number 23-2426 of Winstead PC (referencing matter number 11321-P086WOUS).

If the Examiner has any questions or comments concerning this paper or the present application in general, the Examiner is invited to call the undersigned at (713) 650-2663.

Respectfully submitted,

WINSTEAD PC

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11. K. A. Farley, Nature 376, 153 (1995).
12. ——, S. G. Love, D. B. Patterson, Geochim. Cosmochim. Acta 61, 2309 (1997).
13. S. G. Love and D. E. Brownlee, Science 262, 550 (1993).
14. S. Dermott et al., in Physics, Chemistry and Dynamics of Interplanetary Dust, B. Gustafson and M. Hanner, Eds. (Astronomical Society of the Pacific, San Francisco, CA, 1996), vol. 104, pp. 143–153.
15. D. B. Patterson, K. A. Farley, B. Schmitz, in preparation.
16. S. Asaro and M. Ozima, Nature 317, 520 (1985).
17. I. Premoli-Silva, R. Coccioni, A. Montanari, Eds., The Eocene-Oligocene Boundary in the Marche-Umbria Basin (Italy) (International Union of Geological Sciences, Ancona, Italy, 1988).
18. Limestone samples of ~2.5 g were dried at 90°C overnight, powdered, sieved, and dissolved in 10% acetic acid. After complete decarbonation, the residue was isolated, dried, weighed (to obtain the noncarbonate fraction), and transferred to a tin foil packet. The packet was fused in vacuum, and the evolved He was purified and analyzed by mass spectrometry (11). The estimated analytical uncertainty on [^{3}He] and ^{3}He/^{4}He determinations is <5%. We report [^{3}He] per gram of bulk limestone. In some cases, replicate analyses were made; the mean value is plotted.
19. S. Dermott, P. Nicholson, J. Burns, J. Houck, Nature 312, 505 (1984).
20. F. Marzari, S. Davis, V. Vanzani, Icarus 113, 168 (1995).
21. J. C. Liou, S. F. Dermott, Y. L. Xu, Planet. Space Sci. 43, 717 (1995).
22. P. Weissman, Nature 344, 825 (1990).
23. J. Hills, Astron. J. 86, 1730 (1981); P. Weissman, Earth Moon Planets 72, 25 (1996).
24. M. Rampino and R. Stothers, Nature 308, 709 (1984).
25. J. Luu and H. Zook, Icarus 123, 481 (1996).
26. R. Grieve and E. Pesonen, Earth Moon Planets 72, 357 (1996).
27. S. A. Vishnevsky and A. Montanari, in preparation.
28. O. Pierrard, E. Robin, R. Rocchia, A. Montanari, Geology 26, 307 (1998).
29. J. J. Matese, P. G. Whitman, K. A. Innanen, M. J. Valtonen, Icarus 116, 255 (1995).
30. L. Lanci, W. Lowrie, A. Montanari, Earth Planet. Sci. Lett. 143, 37 (1996).
31. We thank P. Weissman for a constructive and thoughtful review and D. Patterson and K. Robinson for assistance with sample preparation. Supported by NASA and by the David and Lucile Packard Foundation through a fellowship award to K.A.F.

13 January 1998; accepted 27 March 1998

Fullerene Pipes

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Single-wall fullerene nanotubes were converted from nearly endless, highly tangled ropes into short, open-ended pipes that behave as individual macromolecules. Raw nanotube material was purified in large batches, and the ropes were cut into 100- to 300-nanometer lengths. The resulting pieces formed a stable colloidal suspension in water with the help of surfactants. These suspensions permit a variety of manipulations, such as sorting by length, derivatization, and tethering to gold surfaces.

Single-wall carbon nanotubes (SWNTs) of molecular perfection—fullerene nanotubes—are of great interest because of their unique electronic (1) mechanical (2) properties combined with chemical stability. The present availability of various fullerene structures reveals a large gap in the intermediate size range between small spheroidal fullerenes and long SWNTs. This intermediate size range could, however, be of paramount scientific and technological importance. For example, fullerene tubes in the length range of 10 to 300 nm might provide connectors and components for molecular electronic devices. We report here methods that make available, in substantial quantities, fullerene macromolecules occupying this intermediate length range. Our approach involves cutting the nearly endless, highly tangled ropes of nanotubes that are currently available (3, 4) into short lengths of open tubes—fullerene pipes—so they can be suspended, sorted, and manipulated as individual macromolecules.

A vital step in developing the molecular science and technology of these fullerene macromolecules is to take advantage of the rich chemistry available at their ends. We also report here the rational derivatization of these fullerene pipes. The ongoing elaboration of these structures should result in a class of organic molecules with the potential for broad applications.

The SWNTs for this study were prepared by a scaled-up version (5) of the laser-oven method described previously (3, 6). Although this method produces fullerene nanotube material of lower quality (30%) than the previously described method (70 to 90%), it has the advantage of being able to produce 20 g of material in 2 days of continuous operation. This as-grown material contains a substantial fraction of nanoscale impurities (bucky onions, spheroidal fullerenes, amorphous carbon, and others) that are difficult to separate from the nanotubes once they have been cut. For this reason, it became imperative that the starting material be purified before cutting. Previously reported purification methods for multiwalled carbon nanotubes (MWNTs) (7) and SWNTs (8) either totally destroy or are ineffective at purifying the present SWNT material in large amounts. Ultimately, we developed a purification method that consists of refluxing in 2.6 M nitric acid and resuspending the nanotubes in pH 10 water with surfactant followed by filtration with a cross-flow filtration system (9).

Passing the resultant purified SWNT suspension through a polytetrafluoroethylene filter produced a free-standing mat of tangled SWNT ropes—a "bucky paper." Typical scanning electron microscope (SEM) images near and at a torn edge of a paper are shown in Fig. 1, B and C, respectively. As is evident in Fig. 1C, the tearing process produces a substantial alignment of the SWNT ropes. The net yield of purified fullerene fibers from this method depends on the initial quality of the raw material, with typical yields in the range of 10 to 20% by weight. A particularly low-quality starting material (Fig. 1A) was chosen to highlight the efficacy of the method. Survival of such a high percentage of these fibers after refluxing for days in nitric acid is indicative of the high degree of molecular perfection of their sidewalls.

Extensive SEM and transmission electron microscope imaging of the fullerene rope fibers in these purified samples shows them to be highly tangled with one another and so long that their ends are rarely visible. The frequent occurrence of fullerene toroids ("crop circles") in these samples (10) suggests that fullerene rope ends are hard to find because many of the ropes are, in fact, truly endless. We suspect that this condition results from van der Waals adherence of the "live" ends of the ropes to the sides of other ropes as growth proceeds in the argon atmosphere of the laser-oven method. The growing rope ends are then eliminated in collisions with other live rope ends growing along the same guiding rope from the opposite direction. In one dimension, collisions are unavoidable.

We verified that one can cut and make ends from these tangled, nearly endless ropes by several techniques ranging from simply cutting with a pair of scissors to

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APPENDIX I

bombardment with relativistic gold ions. However, a far more effective and efficient method was prolonged sonication of the nitric acid–purified SWNT rope material in a mixture of concentrated sulfuric and nitric acids (3:1, 98% and 70%, respectively) at 40°C (11).

We infer that this method is effective because the collapse of cavitation bubbles in ultrasonication produces microscopic domains of high temperature (12), leading to localized sonochemistry that attacks the surface of the SWNT tubes, leaving an open hole in the tube side. There are previous reports that vigorous sonication in CH_2Cl_2 can damage the sides of MWNTs (13), but the goal here with the SWNT ropes was not just to damage the tubes but to cut them cleanly at the points of damage and separate the cut pieces from the other tubes in the ropes. The advantage of sonicating in the presence of an oxidizing acid is that subsequent attack at the point of damage soon cuts the tube completely. Because at these moderate temperatures the open tube ends are unable to close, continued exposure to the oxidizing acid then slowly etches away the exposed ends, much like the burning of a fuse.

The 3:1 concentrated H_2SO_4:HNO_3 mixture was chosen for the oxidizing acid in this cutting operation because it is also known to intercalate and exfoliate graphite (14). We suspected that it may similarly help to separate the cut tube pieces from the underlying tubes in the rope, thereby exposing these inner SWNTs to new sonication-induced damage and subsequent further cutting. As shown in Fig. 2, the result is efficient cutting of the SWNT rope material into thinned rope pieces and individual cut tubes (15).

To ensure that the cut nanotube pieces were themselves molecularly perfect and chemically clean, we subjected them to further etching in acid without sonication. As expected for open-ended tubes, that is, fullerene pipes, the length distribution shortened systematically with exposure time to the acid. For example, in 3:1 concentrated sulfuric and nitric acid at 70°C, we found that the average cut nanotube shortened at a rate of roughly 130 nm $hour^{-1}$ (Fig. 3). At 70°C in a mixture of concentrated sulfuric acid and 30% aqueous hydrogen peroxide (4:1 by volume), the shortening rate was roughly 200 nm $hour^{-1}$. As advances in sorting nanotubes by helical type are made, it will be interesting to determine whether this etching rate is sensitive to the chiral indices of the nanotubes (n, m), for example, whether all "armchair" tubes $(n = m)$ have a distinct chemistry from "zigzag" tubes $(m = 0)$ and from those of the intermediate helical angle.

The purified SWNT nanotubes flocculated rapidly in aqueous solution, hindering their further manipulation and analysis. We found that stable colloidal suspensions in

Fig. 1. SEM images of (A) raw single-walled fullerene nanotube felt, (B) purified bucky paper, and (C) a torn edge of purified bucky paper. The abnormally low quality of the starting material emphasizes the effectiveness of the purification process.

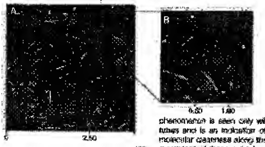

Fig. 2. (A and B) Tapping mode AFM images of cut fullerene nanotubes (pipes) electrodeposited from a stable colloidal suspension onto HOPG. Note the tendency of tubes to align 120° to one another, presumably in registry with the underlying graphite lattice. This phenomenon is seen only with well-purified fullerene tubes and is an indication of a very high degree of molecular cleanness along the tube sides. AFM measurements of these cut tubes show that roughly half have heights corresponding to individual tubes (1 to 2 nm), whereas the rest are aggregates of several tubes in van der Waals contact.

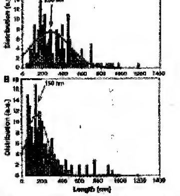

Fig. 3. Size distribution plots of cut nanotubes (A) before and (B) after stirring in a 3:1 mixture of sulfuric and nitric acid at 70°C for 1 hour. The average length before acid treatment was 280 nm (A), and the average length afterward was 150 nm (B). a.u., arbitrary units.

water could be made for cut nanotubes with the assistance of anionic surfactants such as sodium dodecyl sulfate or the nonionic surfactant Triton X-100.

Figure 4 demonstrates the use of these stable nanotube suspensions to achieve a separation by length with field-flow fractionation (FFF) (16), with subsequent analysis by AFM imaging. To ensure that we deposited a representative sample of nanotubes from solution, we developed an electrodeposition technique that drives essentially all nanotubes in suspension onto the surface of highly oriented pyrolytic graphite (HOPG), which was subsequently scanned by atomic force microscope (AFM) (17). This technique relies on the fact that nanotubes readily pick up negative charges in aqueous suspension (18).

As a demonstration of the molecular nature of these cut fullerene pipes, we proceeded to derivatize them at their open ends. Presuming these open ends to be terminated with many carboxylic acid groups as a result of previous treatment in acid (19), we converted these groups to the corresponding acid chloride by reaction with $SOCl_2$ at room temperature. Subsequent

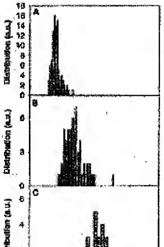

Fig. 4. FFF of cut fullerene nanotube "pipes" in aqueous suspension. (A to C) Nanotube length distributions as measured from AFM images of the suspended fullerene nanotubes electrodeposited on HOPG, as in Fig. 2, for earlier and later FFF fractions.

exposure to NH_2-$(CH_2)_{11}$-SH in toluene at room temperature produced an amide linkage of the nanotube to the alkanethiol. We assayed this chemistry by using the free thiol end to tether the end of the nanotube to a 10-nm diameter gold particle. AFM imaging revealed that most tubes derivatized in this way have a single gold particle bound to at least one of their ends, as demonstrated in Fig. 5. Similar results were obtained regardless of whether the gold particles were exposed to the tubes before or after being deposited on HOPG. Control experiments verified that derivatization was necessary: Gold particles were seldom found at the ends of tubes without alkanethiol tethers. Attachment of such strategically designed binding groups may be very useful in directing assembly of fullerene tubes into molecular devices.

AFM imaging of the cut nanotube pieces on HOPG shows that many are individuals but that many remain in van der Waals contact with each other, perhaps having started as partners in the original rope material. The filtration methods used here discard the most interesting nanotubes: those with lengths substantially less than 100 nm. As we approach this 100-nm length from above, we are beginning to enter the realm of fullerene molecules whose chemistry and physics are dominated by their ends. Although the cut tube pieces made here are open pipes, we expect that they will be

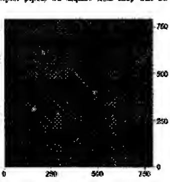

Fig. 5. "Seven minutes to three": an AFM image of two "fullerene pipes" tethered to a common 10-nm-diameter gold sphere. The longer pipe (the minute hand) has another gold particle tethered to its other end. The image was taken after the tubes were electrodeposited onto HOPG from a suspension of a mixture of derivatized tubes with colloidal gold particles (Sigma) in water. The nanotube-to-gold tethers were constructed of alkyl thiol chains attached by amide linkages to open tube ends previously derivatized by converting terminating carboxylic acid groups (arising from the acidic cutting treatment) to the corresponding acid chloride by reaction with $SOCl_2$. Scale in nanometers.

closed by true hemifullerene end caps, forming sealed fullerene capsules, simply by annealing in vacuum at 1000° to 1200°C. The ready rearrangement of carbon sheets to incorporate pentagons, curve, and close at these temperatures is the dominant chemical physics that produces the fullerenes in the first place. Open or closed, these fullerene tubes will have a rich chemistry. They are the fitting subject of a new branch of organic chemistry, a molecular technology of great promise.

REFERENCES AND NOTES

1. S. J. Tans et al., Nature 386, 474 (1997).
2. E. W. Wong, P. E. Sheehan, C. M. Lieber, Science 277, 1971 (1997); B. I. Yakobson and R. E. Smalley, Am. Sci. 85, 324 (1997).
3. A. Thess et al., Science 273, 483 (1996).
4. C. Journet et al., Nature 388, 756 (1997).
5. A. G. Rinzler et al., Appl. Phys. A, in press.
6. T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, R. E. Smalley, Chem. Phys. Lett. 243, 49 (1995).
7. Y. J. Chen et al., Adv. Mater. 8, 1012 (1996); T. W. Ebbesen, P. M. Ajayan, H. Hiura, K. Tanigaki, Nature 367, 519 (1994).
8. K. Tohji et al., J. Phys. Chem. B 101, 1974 (1997); K. Tohji et al., Nature 383, 679 (1996).
9. In a typical procedure, a raw sample of nanotubes (0.5 g) was first refluxed in 1.2 liters of 2.6 M nitric acid for 45 hours. Upon cooling, the solution was transferred to polytetrafluoroethylene centrifuge tubes and spun at 2400g for 2 hours. The supernatant acid was decanted off, replaced by deionized water, and vigorously shaken to resuspend the solids, followed by a second centrifuge-decant cycle. The solids were resuspended in 1.8 liters of water with 20 ml of Triton X-100 surfactant (Aldrich) and adjusted to pH 10 with sodium hydroxide. The suspension was then transferred to the reservoir of a tangential flow filtration system (MiniKros Lab System; Spectrum; Laguna Hills, CA). The filter cartridges used (M22M 600 01N; Spectrum) had mixed-cellulose ester hollow fibers of 0.6-mm diameter, 200-nm pores, and a total surface area of 5600 cm^2. The buffer consisted of 44 liters of 0.2 volume % Triton X-100 in water, of which the first 34 liters were made basic (pH 10) with sodium hydroxide and the final 10 liters were at pH 7. The cartridge inlet pressure was maintained at 5 psi. A control valve was added to the exit so that the outflow rate was restricted to 40 ml min^{-1}.
10. J. Liu et al., Nature 385, 780 (1997).
11. These cut tubes were prepared in a two-step process: cutting and polishing. In a typical example, 10 mg of the purified SWNT "bucky paper" (Fig. 1B) was suspended in 40 ml of a 3:1 mixture of concentrated H_2SO_4/HNO_3 in a 100-ml test tube and sonicated in a water bath (Cole Palmer (Vernon Hills, IL) model 08849-00, 55 kHz) for 24 hours at 35° to 40°C. The resultant suspension was then diluted with 200 ml of water, and the larger cut SWNTs were collected on a 100-nm pore filter membrane (type VCTP; Millipore) and washed with 10 mM NaOH solution. The cut tubes were then further polished by suspension in a 4:1 mixture of concentrated H_2SO_4/30% aqueous H_2O_2 and stirring at 70°C for 30 min. After filtering and washing again on a 100-nm pore filter, the cut nanotubes were suspended at a density of 0.1 mg/ml in water with the aid of 0.5 weight % Triton X-100 surfactant.
12. T. J. Mason and J. P. Lorimer, Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry (Halsted, New York, 1988).
13. K. L. Lu et al., Carbon 34, 814 (1996).
14. B. F. McKay, J. Appl. Phys. 35, 1992 (1964).
15. Taking into account AFM tip broadening, the possibility remains that some of these apparent individual tubes are actually "rafts" of several parallel tubes in van der Waals contact lying on the HOPG surface.
16. A 50-μl sample of cut nanotube suspension (0.07 mg/ml) in 0.5% aqueous Triton X-100 was injected

APPENDIX I

into an FFF instrument (Model F-1000-FO, FFFractionation LLC, Salt Lake City, UT) operating with 0.002% Triton X-100 in water mobile phase at 2 ml min^{-1} and a cross-flow rate of 0.5 ml min^{-1}.

17. Electrodeposition was performed by placing 20 µl of the nanotube suspension on the surface of a freshly cleaved HOPG substrate (Advanced Ceramics, Cleveland, OH), confining the droplet within a viton O-ring (4-mm outer diameter, 1.7 mm thick), capping the trapped suspension with a stainless steel electrode on top of the O-ring, and applying a steady voltage of 1.1 V for 6 min. When suspended in water, the nanotubes are negatively charged and are therefore drawn by the electric field onto the HOPG surface. After deposition, the HOPG-nanotube surface was washed with methanol on a spin coater to remove the water and Triton X-100 surfactant.

18. K. Bubke, H. Gnewuch, M. Hempstead, J. Hammer, M. L. H. Green, Appl. Phys. Lett. 71, 1906 (1997); A. G. Rinzler and R. E. Smalley, unpublished data.
19. K. Kinoshita, Carbon Electrochemical and Physicochemical Properties (Wiley, New York, 1988), pp. 193–201.

20. We thank K. Smith and V. Colvin for helpful discussions. Supported by the NST, the Office of Naval Research, the Advanced Technology Program of Texas, and the Robert A. Welch Foundation.

12 January 1998; accepted 27 March 1998

Cloned Transgenic Calves Produced from Nonquiescent Fetal Fibroblasts

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An efficient system for genetic modification and large-scale cloning of cattle is of importance for agriculture, biotechnology, and human medicine. Here, actively dividing fetal fibroblasts were genetically modified with a marker gene, a clonal line was selected, and the cells were fused to enucleated mature oocytes. Out of 28 embryos transferred to 11 recipient cows, three healthy, identical, transgenic calves were generated. Furthermore, the life-span of near senescent fibroblasts could be extended by nuclear transfer, as indicated by population doublings in fibroblast lines derived from a 40-day-old fetal clone. With the ability to extend the life-span of these primary cultured cells, this system would be useful for inducing complex genetic modifications in cattle.

Research has been in progress for more than a decade to develop a system for genetic modification and large-scale cloning in cattle (1), an important species in agriculture, biotechnology, and human medicine. In the initial work on cloning, embryonic blastomeres were used as donor nuclei because they were thought to be relatively undifferentiated, readily reprogrammed, and likely to support full-term development of the fetus (2). Initial efforts at refining the methodology of nuclear transfer resulted in significant, but limited, improvements in efficiency, and at most, only a few identical calves could be produced from a single donor embryo because of the limited number of cells in the early embryo (3). The next step toward expanding the potential of cloning was the development and use of embryonic stem cells as a source of donor nuclei. Embryonic stem cells are derived from the inner cell mass of an early embryo and are thought to be relatively undifferentiated. In addition, mouse embryonic stem cells divide indefinitely in culture without differentiation and can be readily genetically modified (4). Embryonic stemlike cells have been developed in the bovine (5) and have been used as a source of donor nuclei in nuclear transfer, but they only supported development of fetuses to 60 days in vivo (6). To date, a source of cells that can be used for genetic modification and large-scale cloning in cattle has not been found.

Other research in nuclear transplantation has shown that the cell cycle stage of the donor cell affects the extent of development of the embryo after nuclear transfer. When the donor cell is fused to the recipient oocyte, which is arrested in the second metaphase in meiosis, the nuclear envelope breaks down and the chromosomes condense until the oocyte is activated (7). This condensation phase has been shown to cause chromosomal defects in donor cells that are undergoing DNA synthesis (7). Donor cells in the G_1 phase of the cell cycle (before DNA synthesis), however, condense normally and support a high rate of early development (7).

In previous work in the sheep, it was suggested that arrest in G_0 (by serum starvation) was the key in allowing donor somatic cells to support development of embryos to term (8).

Our rationale in selecting an optimal donor cell for nuclear transplantation was that the cell should not have ceased dividing (which is the case in G_0) but be actively dividing, as an indication of a relatively undifferentiated state and for compatibility with the rapid cell divisions that occur during early embryo development. The cells should also be in G_1, either by artificially arresting the cell cycle or by choosing a cell type that has an inherently long G_1 phase. We chose fibroblasts from fetuses because they can grow rapidly in culture and have an inherently long G_1 phase (9).

Fetal fibroblasts were isolated from a day 55 male fetus (Fig. 1A), cultured in vitro, and passaged twice before being transfected with a marker construct consisting of a β-galactosidase–neomycin resistance fusion gene driven by a cytomegalovirus (CMV) promoter (pCMV/β-GEO) (10). Cells were selected with neomycin for 2 weeks, and five neomycin-resistant colonies were isolated and analyzed for stable transfection by polymerase chain reaction (PCR) amplification of a segment of the transgene (11) and by assay of β-galactosidase activity. Colony CL1 was chosen for nuclear transfer experiments. These fibroblast cells

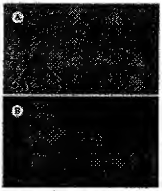

Fig. 1. Transgenic fetal fibroblast CL1-5 used for nuclear transplantation (A) phase contrast (× 100). (B) Labeling of CL1-5 fibroblast cell line with PCNA monoclonal antibody (Sigma, St. Louis, MO) and FITC-conjugated secondary antibody (magnification × 200).

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